

DOCKET NO.: M&M-033-USA-PCT
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

#14
03/11/03
AS

In re application of

H. FUKUI, et al.

Serial Number: 09/719,166

Art Unit: 1711

Filed: DECEMBER 13, 2000

EXAMINER: SANZA L MCCLENDON

FOR: CATIONIC PHOTOCATALYST COMPOSITION AND
PHOTOCURABLE COMPOSITION

DECLARATION UNDER 37 CFR 1.132

Honorable Commissioner
of Patents and Trademarks
Washington, D.C. 20231

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MAR 13 2003

TC 1700

Sir:

I, Hiroji Fukui, a citizen of Japan residing at 8-316, Hattanda-cho, Kisshoin, Minami-ku, Kyoto-shi, Kyoto 601-8325 Japan, hereby declare and state:

1. I graduated from Kyoto University, Engineering Research Division in March 1992 and graduated from the second term of the doctor course in March 1995. I have entered SEKISUI CHEMICAL CO., LTD. in April 1995. I have been engaged in development of an acrylic pressure-sensitive adhesive and further engaged in development of photocurable pressure-sensitive adhesive.

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3. Articles:

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Adhesives with UV Cationic Curing of Epoxy Resins.

Authors: FUKUI H, ISHIZAWA H, NAKASUGA A

(SEKISUI CHEMICAL CO., LTD., KYOTO, JPN)

Journal: J. Photopolym. Sci. Technol., VOL. 12, NO. 1

PAGE. 169 - 172, 1999

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Journal: J Polym Sci Part A, VOL. 32, NO. 14 PAGE. 2699 - 2708 1994

4. I am a co-inventor of the above-captioned application and have read and understand the claims.

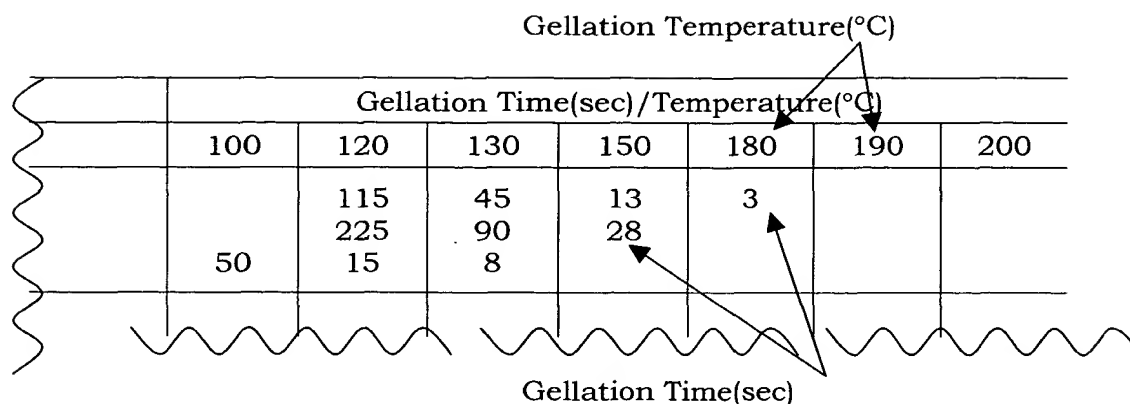
Affidavit

I, the undersigned, Hiroji Fukui swear an affidavit of the following contents with respect to the specification of US Patent Application Serial No. 09/719,166.

(1) The "low catalytic activity" of a catalyst included in the claims of the present application means that the catalyst has an extremely low activity or practically no catalytic activity at a temperature in the range of 20°C to 80°C. Since in a composition of the present invention containing this catalyst and a compound having an epoxy group, an activity of the above catalyst has an extremely low activity or no activity in the range of 20 to 80°C, the composition is practically not cured or not gelated. That is to say, a catalytic activity with which the above composition is practically not cured or not gelated is called a "low catalytic activity".

A proton is generated due to thermal decomposition of the catalyst itself and thus generated proton is added to an epoxy group to thereby reveal the activity of the above catalyst. After the proton is added to an epoxy group, an active species is generated that can attack an epoxy group to thereby drive a reaction of an epoxy group like a chain reaction. As a result, polymerization or a crosslinking reaction increasing a molecular weight is performed to cause gelation. A liquid composition is thereby gelated and cured into a solid.

(2) "Gelation Time (sec)/Temperature (°C), which is a unit used in Table 3 of the document in Japanese entitled "Curing of Epoxy Resins Using Novel Sulfonium Salts," which was submitted previously, is a unit for a gelation time measured in sec at a given temperature. The table is to be interpreted as follows. For example, 180 and 190 below indicate temperatures and "3" and "28" indicate a gelation time. That is to say, it is shown that a gelation time is 3 sec at a temperature of 180°C.



		Gellation Temperature(°C)						
		Gellation Time(sec)/Temperature(°C)						
		100	120	130	150	180	190	200
			115	45	13	3		
			225	90	28			
	50		15	8				

The meaning of a gelation time of an epoxy group containing resin using a thermodecomposable onium salt cationic catalyst is as follows: An onium salt is at first thermally decomposed in an epoxy group containing resin to produce a proton. Then, the proton attacks an epoxy group to cause a chain reaction of epoxy groups, that is a ring opening polymerization. In a case where the resin with two or more epoxy groups that is used in the above article, this chain reaction is in progress and at the same time not only does a ring opening polymerization make progress, but also a crosslinking reaction arises. As a result, a solvent-insoluble gel is produced. The time consumed for production of the solvent-insoluble gel is the gelation time.

Accordingly, the gelation time is an evidence to prove occurrence of a reaction of epoxy groups. If a pressure-sensitive adhesiveness is extremely low and the composition has been cured like a plastic, this phenomenon is called "cure".

When the above series of reactions is evaluated with a thermal analysis apparatus, there are observed, in addition to an endothermic phenomenon accompanied with a phase transition, an exothermic phenomenon due to thermal decomposition of an onium salt and an exothermic phenomenon due to a chain reaction (a ring opening polymerization) of epoxy groups. In fact, the exothermic phenomena are referred to in an example of a prior art, Lamanna et al (U.S. Patent 5,554,664), cited on in examination of the present patent application.

In contrast thereto, a composition relating to the present invention has no exothermic peak in a DSC data chart at least at a temperature in the range of 20 to 80°C.

Furthermore, in Table 3 of the above article, description is given that gelation occurs in a composition containing an epoxy resin A, which is a bisphenol A type epoxy resin, a compound 2a and phenyl glycidyl ether in a time of 115 sec. at 120°C. Furthermore, in Table 6 of the above article, observation is made on storage stability at 40°C, which reveals a fact that gelation occurs on the fourth day from the start of storage. Accordingly, the compound 2a has an activity at a temperature in the range of 20 to 80°C.

Moreover, in Table 3 of the above article, description is given of no data concerning the compound 2b, but of data concerning a compound 2f is described. There is shown that the compound 2f as well has a thermocatalytic activity at a temperature of 40°C, similar to the case of the compound 2a.

The undersigned hereby declares that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

signed this 20th day of February, 2003

Hiroji Fukui

Hiroji Fukui



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I, the undersigned, Hiroji Fukui swear an affidavit of the following contents with respect to the specification of US Patent Application Serial No. 09/719,166.

The Examiner stated that the salt D shown in Table 3 of Lamanna et al. has low activity at lower temperature range such as 20 to 80°C.

The salt D, however, has sufficient activity at 20 to 80°C. Particularly, as shown from Table 2 of Lamanna et al., calorific power at peak 1 is 35.6J/g, while the amount at peak 2 is 307.7 J/g. A coefficient of reaction is generally proportional to a calorific power, if a reaction matrix is the same. In Example 5, the reactions are completed at heat production at peaks 1 and 2, respectively and experiments confirming peaks 1 and 2 are successive operations. Thus, the coefficients of reaction as to respective peaks 1 and 2 are as follows:

The coefficient of reaction as to peak 1 is $35.6/(35.6+307.7) \times 100 = 10.4\%$

The coefficient of reaction as to peak 2 is $307.7/(35.6+307.7) \times 100 = 89.6\%$

As described above, the reaction sufficiently occurs within a range of 48 to 60°C and the salt D has catalytic activity in the reaction showing peak 1.

By contrast, the present claimed onium salt has not such sufficient activity within a range of 20 to 80°C.

We enclose herewith experimental data to support our arguments described above. The data are DSC charts of a composition A and B as shown in table 1 below.

Table 1

	Composition A	Composition B
EPICOAT828 (=EPON828)	100phr	100phr
BEO-60E (=SYN FAC8024)		40phr
SP-170	2phr	1.4phr

The composition A is that of Comparative Example 1 described in the text of the present application. Composition B is prepared in accordance with Example 5 of Lamanna et al. except that an onium salt SP-170, which is used in the present invention, is used as the catalyser. The temperature elevation rate is set to be 10°C/min., namely the same rate as in Lamanna et al. and measurements are performed within a range of 20 to 80°C.

A result is shown in the attached sheet. As shown in the attached data, there is no peak in DSC charts of compositions A and B.

Meanwhile, as described in Lamanna et al. Example 2 of Lamanna et al. shows clear peaks within a range of 20 to 80°C. Comparison of the result of Composition A and B with the result of Example 2 of Lamanna clearly shows that the present claimed onium salt has extremely low or no catalytic activity within a range of 20 to 80°C, while the salt of Lamanna et al. has sufficient activity enough to show such DSC peak within a range of 20 to 80°C.

In view of our comments and the experimental data, it is clear that the salt D of Lamanna et al. has sufficient activity within a range of 20 to 80°C.

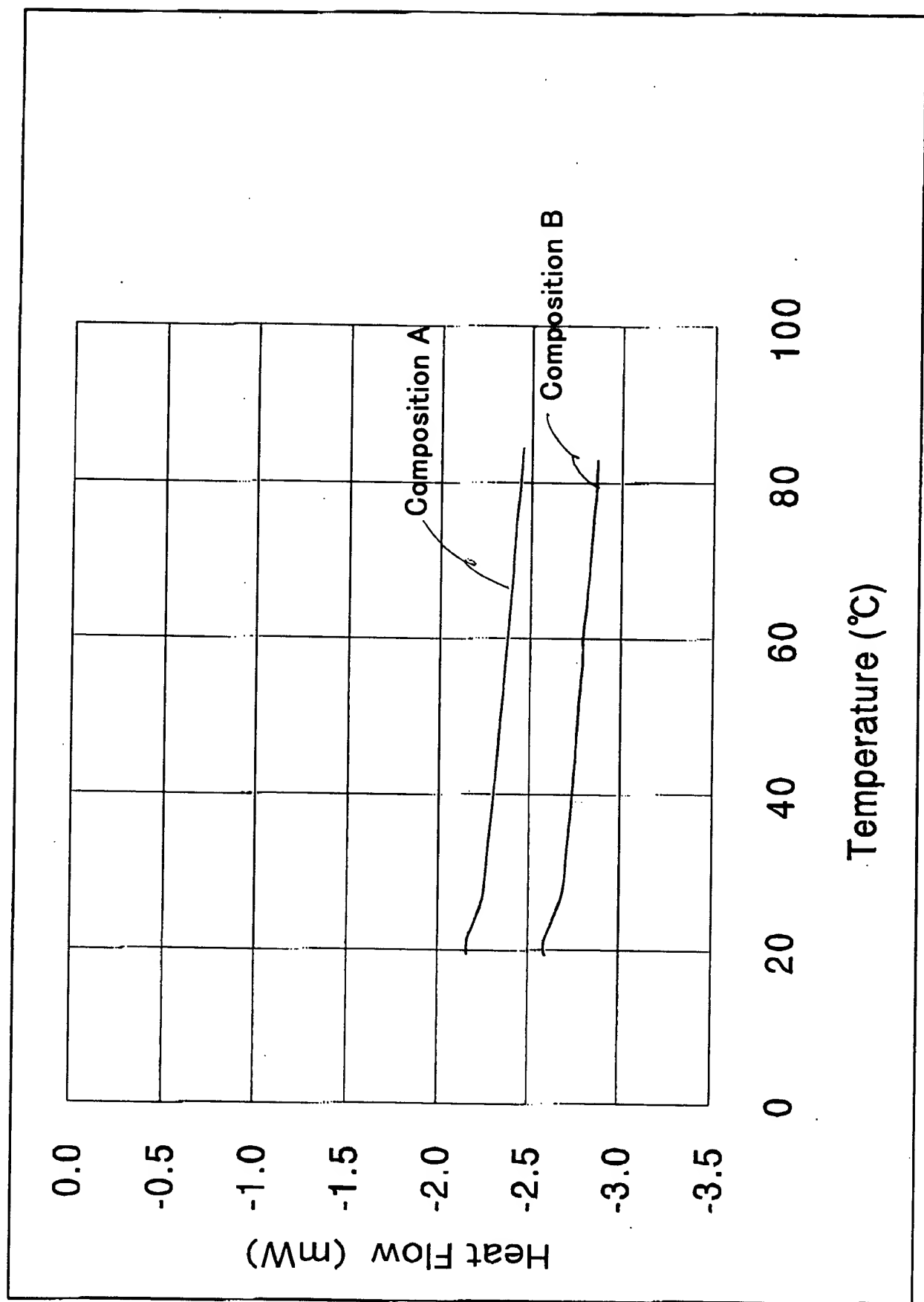
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validity of the application or any patent issued thereon.

signed this 20th day of February, 2003

Hiroji Fukui

Hiroji Fukui





DECLARATION

**I, Chikara Miyazaki, c/o MIYAZAKI & METSUGI, of Nishimura Building,
6-5, Tanimachi 1-chome, Chuo-ku, Osaka, Japan certify that I am the translator of
the documents in the Japanese language, "CURING OF EPOXY RESINS USING
NOVEL SULFONIUM SALTS / CURING BY MEANS OF THERMALLY
LATENT AND PHOTOLATENT CURING CATALYSTS /", attached hereto and
that to the best of my knowledge and belief the following is a true and correct
translation thereof.**

**RECEIVED
MAR 13 2003
TC 1700**

January 27, 2003

C. Miyazaki

CURING OF EPOXY RESINS USING NOVEL SULFONIUM SALTS/ CURING BY
MEANS OF THERMALLY LATENT AND PHOTOLATENT CURING CATALYSTS/

Fumio Hamatsu*, Toshikazu Takada*, and Isao Endo*

* Chemical Resources Laboratory, Tokyo Institute of Technology
4259 Nagatsuka, Midori-ku, Yokohama 227

Abstract

The performance of p-substituted phenylbenzylmethylsulfonium salts and p-substituted phenyldimethylsulfonium salts as thermally latent and photolatent curing catalysts was evaluated using epoxy resins (bisphenol A diglycidyl ether and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate).

Studies of the curing reactions of epoxy resins using these catalysts have shown that p-hydroxyphenylbenzylmethylsulfonium salts (2a) and p-hydroxyphenyl-p-nitrobenzylmethylsulfonium salts (2f) with a phenol structure on their sulfur atom exhibit higher activities under heating conditions than benzyltetramethylenesulfonium salts (1) and offer activities even under UV irradiation. However, one-component compositions of these compounds with epoxy resins have been found to lack storage stability at room temperature and require storage in a dark place.

On the other hand, p-hydroxyphenyldimethylsulfonium

salts (3a), p-acetoxyphenyldimethylsulfonium salts (3b) and p-methoxycarbonyloxyphenyldimethylsulfonium salts (3c) showed a low activity under heating conditions compared with 1. Although they also exhibited low activities under UV irradiation, the epoxy resins underwent the progress of curing. Furthermore, one-component compositions using 3a to 3c showed high storage stability in a dark place and were found to act as good thermally latent and photolatent curing catalysts.

1. Introduction

Latent catalysts, which do not initiate polymerization under normal conditions such as room temperature and indoor lighting and which show activities only after exposed to specific external stimuli such as heating or UV irradiation, are industrially effective, and some of them are already actually used as curing catalysts for epoxy resins ¹⁻⁵⁾. In curing of epoxy resins, such latent catalysts have a merit of being capable of having one-component with main agents and are greatly expected to act as catalysts of good properties. However, there are still very few thermally latent curing catalysts of high activity and latency, that is, catalysts capable of sufficient curing in a few amount of heat and also having a long usable time period, and none of them are satisfactory.

On the other hand, for a dozen of years or so UV cured

resins have been focused in terms of resource saving, environmental conservation and so forth. They are widely commercialized in the fields of inks, paints and adhesives, and of them acrylate-based oligomers are mainstream. These resins, however, cause the problems of contraction during curing and oxygen inhibition in the air. For the conquest of these shortcomings, use of epoxy resins themselves as UV cured resins has recently been studied. Even in this viewpoint, it is desirable to develop photolatent curing catalysts that can generate high sensitive, excellent photolatent cationic species ^{1, 4, 6-11}).

In order to improve the activity of benzylsulfonium salts (1) ^{3, 12-14}) that functions as a thermally latent catalyst, we have synthesized benzylmethylsulfonium salts (2a) with a phenol structure on its sulfur atom, and have shown that 2a acts as a thermally latent catalyst, the activity of which is higher than that of 1, in the ring opening polymerization of phenylglycidyl ether (hereafter, abbreviated as PGE), a model compound of an epoxy resin using 2a ¹⁵). In addition, to discuss the relationship between its activity and structure, we synthesized a variety of benzylsulfonium salts (2) ^{16, 17}) and dimethylsulfonium salts (3) ^{18, 19}), polymerized PGE using these salts, and showed the importance of the benzyl group and aromatic ring on the sulfur.

In this report, we showed the evaluations of activities

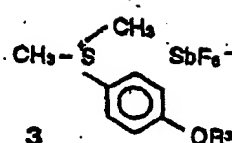
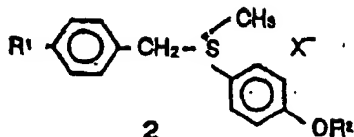
of the sulfonium salts (2, 3) using general-purpose liquid epoxy resins in order to apply as curing catalysts for epoxy resins sulfonium salts whose thermal latency and photolateness had been confirmed in a model system using PGE. We also discussed the utility of these salts as thermal latent curing catalysts or photolateness curing catalysts by evaluating the measurements of storage stability in one-component states as well as basic physical properties of cured materials obtained.

2. Experiments

2.1 Samples

Sulfonium salts were synthesized from p-hydroxyphenyldimethylsulfide or tetrahydrothiophene in accordance with the previous reports ^{3, 12, 15-17}). Bisphenol A Epoxy Resin (hereafter, abbreviated as Epoxy Resin A, molecular weight 380, Epicoat 828, epoxy article from Yuka Shell) and Alicyclic Epoxy Resin (hereafter, abbreviated as Epoxy Resin B, molecular weight 252, Seroxide 2021, available from Daicel Chemical Industries, Ltd.) were used as liquid epoxy resins, and PGE (industrial grade, from Kishida Chemical Co., Ltd.) and propylene carbonate (hereafter, abbreviated as PC, reagent grade, from Kishida Chemical Co., Ltd.) as diluting agents for the preparation of catalyst solutions. The structures of the sulfonium salts used are given in Table 1.

1) Sulfonium salts



	2a	2b	2c	2d	2e	2f
R ¹	H	H	H	H	OH ₂	NO ₂
R ²	H	H	CH ₂ O(O)	CH ₂ OO(O)	H	H
X	SbF ₆	PF ₆	SbF ₆	SbF ₆	SbF ₆	SbF ₆
mp (°C)	114.0 ~116.0	138.0 ~140.0	115.0 ~117.0	72.0 ~75.0	138.5 ~139.0	167.0 ~168.0

	3a	3b	3c
R'	H	CH ₃ O (O)	CH ₃ OC (O)
mp (°C)	171.0 ~172.0	153.0 ~155.0	140.0 ~141.5

2) Epoxy resins

$$\text{H}_2\text{C}-\underset{\text{O}}{\underset{\text{O}}{\text{CH}}}-\text{CH}_2 \left\{ \text{O}-\text{C}_6\text{H}_4-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{C}_6\text{H}_4-\text{O}-\underset{\text{OH}}{\text{CH}}-\text{CH}_2 \right\}_{0.1} \text{O}-\text{C}_6\text{H}_4-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\underset{\text{O}}{\underset{\text{O}}{\text{CH}}}-\text{CH}_2 : \text{Epoxy resin A}$$
O=C1C=CC(OC2=CC=CC=C2)CC1 ; Epoxy resin B

Into a mortar was paced 97 parts by weight of Epoxy Resin A and 3 parts by weight of sulfonium salts and the resulting material was sufficiently mixed and dispersed with pestle and then was subjected to vacuum deaeration for 30 minutes. The gellation times of the heterogeneous composition thus obtained at various temperatures were measured using a gellation test device GT-JIS type (manufactured by Nissin Chemical Co., Ltd.) according to JIS C2104. For some sulfonium salts, a catalyst solution prepared in advance by mixing a sulfonium salt (1 part

by weight) with PGE or PC (2 parts by weight) at room temperature was added in specified parts by weight to 100 parts by weight of Epoxy Resin A or B to yield a homogeneous liquid composition. The gellation time of the composition was determined by a similar method.

2.3 DSC Measurement of Epoxy Resin Compositions

A composition was obtained by adding 1.5 parts by weight of a catalyst solution prepared by mixing 2 parts by weight of PC with 1 part by weight of a sulfonium salt, to 100 parts by weight of Epoxy Resin A or B. The composition (10 mg) was placed in an enclosed aluminum pan and was subjected to DSC measurements by means of a thermoanalyzer Model SSC-5000 (manufactured by Seiko Instruments Inc.) at a rate of temperature rise of 10°C/min.

2.4 Measurement of Pot Life

An epoxy resin composition was prepared by adding a catalyst solution consisting of 12 parts by weight of PGE and 1 part by weight of a sulfonium salt to 88 parts by weight of Epoxy Resin A. Also, another epoxy resin composition was produced by the addition of a catalyst solution of 2 parts by weight of PC and 1 part by weight of a sulfonium salt to 100 parts by weight of Epoxy Resin B. These compositions were stored at a specified temperature in a dark place and subjected

to viscosity measurements at 25°C by given storage time period using a B type viscometer Model BL (manufactured by Tokimec).

2.5 Physical Property Measurements of Cured Materials

2.5.1 Curing and Molding

A composition was obtained by adding a given amount of a catalyst solution of 2 parts by weight PGE and a 1 part by weight sulfonium salt, to Epoxy Resin A. This composition was vacuum deaerated for 30 minutes at room temperature, poured into a mold at a specified temperature and cured at a given temperature for a given time using a table press Model EH (manufactured by Toyo Seiki Seisaku-sho, Ltd.) to produce cured test specimens of 100 mm × 10 mm × 4 mm.

2.5.2 Hardness

The hardnesses of the cured materials were measured using a Rockwell type hardness tester Model DRH-M (manufactured by Toyo Seiki Seisaku-sho, Ltd.) on the M scale (using a steel sphere with an indentater of 6.350 cm in diameter).

2.5.3 Bending Strength and Bending elastic modulus

The bending strength and the Bending elastic modulus of a cured material were determined by means of a strength tester Strograph Model M-2 (manufactured by Toyo Seiki Seisaku-sho).

2.5.4 Water Absorption Ratio

A cured material was placed in a test tube filled with purified water in accordance with JIS K6911 and was immersed in a thermostatic water bath set at 23°C for 24 hours. The water absorption ratio was calculated from the weight difference before and after the testing.

2.6 Measurement of Photo-Curing Energy

A composition obtained by adding 4.5 parts by weight catalyst solution (sulfonium salt/PC = 1/2) prepared by mixing a sulfonium salt and PC to 100 parts by weight Epoxy Resin B, was applied to a hard vinyl chloride plate with a spin coater so that the thickness was about 5 μm . This was irradiated with UV light using a GS miniconveyor type ultraviolet irradiation apparatus fitted with a 80 W/cm (2 KW) high-pressure mercury lamp (manufactured by Japan Storage Battery) (the distance between the lamp and the plate is 8 cm), and the amount of irradiation (mJ/cm^2) until the tack of the applied material disappeared was determined.

3. Results and Discussion

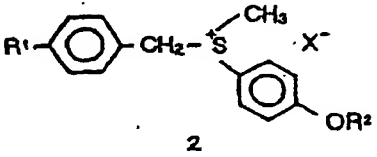
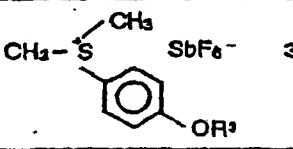
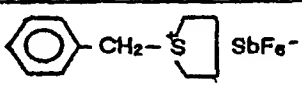
3.1 Evaluation of the Compositions as Thermal Latent Curing Catalysts

3.1.1 Gellation time

First, the gellation time of Epoxy Resin A composition

containing 3 % by weight of sulfonium salt was measured for the evaluation of each sulfonium salt for its catalyst activity under heating conditions. The results are given in Table 2.

Table 2 Gellation time of heterogeneous epoxy compositions with various sulfonium salts by thermal curing.

Sulfonium salt		Gellation time (sec)					
		Temperature(°C)	80	100	120	150	180
 2	2a; R ¹ =H, R ² =H, X=SbF ₆	>1800	480	70	8	1	
	2b; R ¹ =H, R ² =H, X=PF ₆			>1000	170	20	
	2c; R ¹ =H, R ² =CH ₃ C(O), X=SbF ₆	170	63	27	2	1	
	2d; R ¹ =H, R ² =CH ₃ OC(O), X=SbF ₆	117	26	6	1		
	2e; R ¹ =CH ₃ , R ² =H, X=SbF ₆	1200	250	65	4	1	
	2f; R ¹ =NO ₂ , R ² =H, X=SbF ₆		>1800	390	48	17	
 3	3a; R ¹ =H				>1800	195	
	3b; R ¹ =CH ₃ C(O)			>1800	510	125	
	3c; R ¹ =CH ₃ OC(O)			>1800	270	70	
 1				>1800	170	45	

Composition : Epoxy resin A / Sulfonium salt = 97 / 3

These results show that benzylmethylsulfonium salt (2a) having a phenol structure on its sulfur atom exhibits a relatively high activity compared with that of 1; however, dimethylsulfonium salt (3a) having a methyl group in place of a benzyl group offers a comparatively lower activity than those of 2a and 1. Thus, the presence of both a benzyl group and phenol structure on the sulfur atom is thought to play an important

role for the activity of a sulfonium salt as a thermal curing catalyst. Comparisons of gellation times between 2a and 2e and 2f as well as 2a and 2c and 2d reveal that the activity of 2a is enhanced by the introduction of an electron donor group onto the benzene ring of the benzyl group or the incorporation of an electron attractive group onto the phenol structure portion.

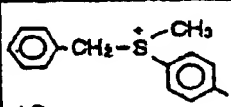
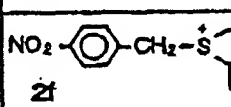
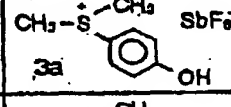
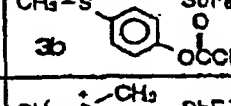
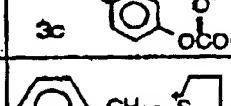
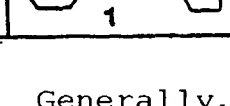
These effects caused by the substitution groups indicate that the cation species that triggers the curing reaction of an epoxy resin is the benzyl cation in this system. This benzyl cation is probably generated through the S_N1 mechanism, and thus the more the formed benzyl cation is stabilized, the higher the activity. This result is similar to the case where PGE, a model compound, is used ¹⁷⁾. In addition, comparison between 2a and 2b indicates that pair anions show a high activity in the case of SbF_6 with lower nucleophilicity. This pair-anion dependency is also in good agreement with the result of the single polymerization of PGE.

On the other hand, while the introduction (3b, 3c) of an electron attractive group onto the aromatic ring of 3a enhanced the catalyst activity in the experiment using PGE, the case using Epoxy Resin A produced a similar effect, and the activity of 3c is comparable to that of 1.

Incidentally, the catalyst in the composition used in this test was not dissolved at room temperature and was in a heterogeneous dispersed state. Also, in gelated states there

were some sulfonium salts that were not completely dissolved. Preparation of a composition using a thermal latent curing catalyst having a liquid epoxy resin as the main agent, requires easy production of a homogeneous composition at room temperature without heating. As such, for some sulfonium salts, they were made dissolved in PC or PGE, a reaction dilution agent, in advance, and then this catalyst solution was added to Epoxy Resin A or B to yield a homogeneous composition, which was subjected to gellation testing (Table 3).

Table 3 Gellation time of homogeneous epoxy compositions with various sulfonium salts by thermal curing.

Composition (weight ratio)			Gellation time (sec) / Temperature (°C)						
Epoxy resin	Sulfonium salt	Diluent	100	120	130	150	180	190	200
A (97) A (100) B (100)	 2a	(1) PGE (2) PC (2)		116 225 60	45 90 8	13 28	3		
A (100) B (100)	 2f	(1) PC (2) PC (2)			610 25	140 7			
A (100) B (100)	 3a	(1) PC (2) PC (2)					480 22	315 14	170
A (100) B (100)	 3b	(1) PC (2) PC (2)					230 13	145 8	
A (100) B (100)	 3c	(1) PC (2) PC (2)					200 9	125 6	
A (100) B (100)	 1	(1) PC (2) PC (2)		135	65	330 20	75	43	

Generally, the temperature of curing Epoxy Resin B is

lower than that of curing Epoxy Resin A. In this case as well, the gellation time was shorter in Epoxy Resin B than in Epoxy Resin A at the same temperature in any sulfonium salts. For example, a composition containing a catalyst solution of 2a and PC and Epoxy Resin A and another composition containing a catalyst solution of 2a and PC and Epoxy Resin B had gellation times of 225 seconds and 15 seconds, respectively, at 120°C, and thus the latter gellated faster by 15 times than the former. The order of activities of sulfonium salts based on the gellation time was the same as the case of the heterogeneous system and was $2a > 2f > 1 > 3c > 3b > 3a$. In addition, the amount of catalyst used in this homogeneous composition was smaller than that in the previous heterogeneous case, and therefore each required a long gellation time for the same temperature.

3.1.2 Effects of the Amount of Catalyst

The sulfonium salt is a catalyst that is different from amine-based curing agents of a polyaddition reaction type and from acid anhydrous curing agents, and so the equivalent required for curing does not exist. A small amount of it can bring about the ring opening polymerization of the epoxy ring leading to curing. Thus, catalyst solutions (sulfonium salt/PC = 1/2) prepared by dissolving 2a, 2f, 3b, and 3c in PC each were added to 100 parts by weight of Epoxy Resin A in such a way that the sulfonium salt was in an amount of 0.1 to 1.5

part by weight, to prepare compositions. The gellation times of the compositions were measured at a specified temperature Fig. 1).

As a result, although any of the sulfonium salts show almost constant gellation times when the amounts of them are 0.75 phr or more, when 0.75 phr or less, the gellation times are drastically prolonged, so that the gellation time for 0.1 phr is 6 to 9 times that for 1 phr. In addition, the curves clearly show that benzylmethylsulfonium salt (2a) is more active than dimethylsulfonium salts (3b, 3c). Therefore, 2a seems to be capable of rapidly curing epoxy resins in an amount of 1 phr or less.

3.1.3 Evaluations of Thermal Latency and Curing Initiation Temperature

For the evaluation of latency that is a key for the thermally latent curing catalyst and the estimation of the optimal temperature necessary for actually curing and forming the epoxy resin, 1.5 parts by weight PC solutions (PC/sulfonium salt = 2/1) of sulfonium salts each were added to 100 parts by weight Epoxy Resin A or Epoxy Resin B to yield compositions. The composition was subjected to DSC measurement at a rate of temperature rise of 10°C/min. Figs. 2 and 3 illustrate the results.

Compositions from Epoxy Resin B each show an exothermal

curve of a relatively sharp, nearly single peak except 2b (Fig. 3), while the compositions from Epoxy Resin A each show two exothermal peaks with a comparatively wide exothermal temperature width (Fig. 2).

Evaluations of the slopes of rising-up of the exothermal curves in Fig. 3 have revealed that 2a exhibits the highest latency and its heat liberation initiating temperature (T_s) is 89°C.

On the other hand, it has been shown that 2b whose pair anion is PF_6 starts to liberate heat at the same temperature as 2a, that the slope of the rising-up is slightly small, and that the latency is scarce. It is also shown that 2f starts to liberate heat at 100°C as well, while any of the dimethylsulfonium salts (3) require relatively high temperatures of 130°C and more for the start of polymerization. Table 4 illustrates T_s values obtained from the DSC curves, the maximum heat liberation temperatures (T_p) and the heat liberation completion temperatures (T_e). The T_p values suggest that heating at about 140°C or more for Epoxy Resin A and at about 120°C or more for Epoxy Resin B is suitable to cure the compositions using 2a in a short time.

Table 4 DSC analyses of mixtures of epoxy resins and sulfonium salts.

Epoxy resin ^{a)}	Sulfonium salt ^{a)}	T _s (°C)	T _p (°C)	T _e (°C)
A	2a	88	146	268
	2f	88	182	276
	2a	148	251	283
	3b	140	235	271
	3c	142	233	271
B	2a	89	123	259
	2b	89	144	— ^{b)}
	2f	100	140	259
	3a	149	197	249
	3b	133	175	237
	3c	132	170	231

a) Epoxy resin / PC / Sulfonium salt = 100 / 1 / 0.5

b) Exothermic reaction didn't terminate below 300°C.

3.1.4 Physical Properties of Cured Materials

Evaluations of activities using PGE of the previous reports¹⁵⁻²⁰⁾ and the results of gelation times and DSC measurements of this report show that 2a is the catalyst that is expected to have the highest activity as well as storage stability in the one-component state. As such, compositions obtained by adding a catalyst solution of 2a and PGE to Epoxy Resin A were cured and molded under various conditions, and the cured materials thus obtained were subjected to measurements of hardness, flexural strength, flexural modulus and water

absorption ratios (Table 5).

Table 5 Properties of cured epoxy resins.

Composition (weight ration)			Curing condition		Hardness (M)	Flexural strength (kg/mm ²)	Flexural modulus (kg/mm ²)	Water absorption ratio (%)
PGE	2a	Epoxy resin A	Temp. (°C)	Time (h)				
3.0	1.5	95.5	130	0.5	103	5.0	316	0.09
2.0	1.0	97.0	110	0.5	98	8.3	195	0.19
			120	0.5	102	8.8	300	0.13
			130	0.5	106	8.9	305	0.12
			100	2	96	10.6	248	0.14
			120	2	97	5.4	296	0.17
			170	3	108	8.9	391	0.11
0.8	0.4	98.8	140	2	83	— ^{a)}	— ^{a)}	0.09
			150	2	102	5.6	353	0.11
			170	7	106	5.6	308	0.14
CP-66 ^{b)} 1.5		98.5	150	2	78	— ^{a)}	— ^{a)}	0.16
			200	3	107	8.4	301	0.23

a) Could not break

b) Thermally latent catalyst manufactured by Asahi Denka Kogyo K. K.

As a consequence, the cured material obtained by curing the composition using 1 % by weight of 2a at 110°C for 0.5 hour exhibits a slightly small elastic modulus and has a water absorption ratio smaller than others, suggesting that unreacted epoxy groups are present in its cured material due to the lack of curing time. On the other hand, materials obtained by curing at 130°C for 0.5 h and at 170°C for 3h exhibit almost the same values in physical properties measured, showing good qualities. Additionally, a material produced by curing the composition

using 1.5 % by weight of 2a at 130°C for 0.5 h shows the smallest water absorption ratio and a small flexural strength leading to brittle property. Furthermore, the cured material is brown, showing that the curing in these conditions is inappropriate.

On the other hand, a composition using 0.4 % by weight of 2a required a certain amount of curing time, giving a good cured material at 150°C for 2h or more. In addition, for comparison, Epoxy Resin A was cured using CP-66 (manufactured by Asahi Denka Kogyo K.K.) commercially available as a thermally latent curing catalyst. As a result, the curing requires 200°C and the 3-h time period for acquiring levels of properties similar to those of the composition obtained by curing the composition using 1 % by weight of 2a at 130°C for 0.5 h, affirming that 2a is considerably high in activity compared with CP-66.

3.1.5 Storage Stability

Another important property of the thermally latent curing catalyst in addition to high latency and high activity is storage stability (pot life) of a composition containing a main agent in a one-component state. Benzylmethylsulfonium salts (2c, 2d) having an acetoxy group or methoxycarbonyloxy group in place of the p-site hydroxyl group of the phenol portion and 2e having a methyl group at the p-site of the benzene ring of the benzyl group can start to be polymerized at 40°C or lower,

which have been confirmed from the result of PGE polymerization^{16, 17)}, and thus their storage stability seems to be low. Incidentally, as described above, benzylmethylsulfonium salt (2a) has high activity and latency, and dimethylsulfonium salts (3a, 3b, 3c) are also expected to have high storage stability higher than that of 2a. Hence, one-component compositions having Epoxy Resins A and B as main agents were stored at a constant temperature in a dark place and subjected to measurements of viscosity by given time at 25°C to evaluate the storage stability from the viscosity change. The results are shown in Fig. 4 and Table 6. Fig. 4, illustrating the storage stability of a composition prepared by the addition of 2a to Epoxy Resin A, clearly indicates that keeping a one-component composition at 20°C in a dark place leads to an about 3-week pot life (time period when the viscosity is kept to be twice or less the initial viscosity) and keeping at 10°C results in a pot life of 2 months or more; however, storing at a temperature higher than the temperature leads to poor storage stability and at 40°C it resulting in gellation only in third day. In addition, 2f causes gellation in 20th day. On the other hand, compositions prepared by use of dimethylsulfonium salts (3a, 3b, 3c) in Epoxy Resin A are excellent in storage stability even at 40°C and their viscosities in 2 months remain 1.05, 1.22 and 1.85 times the initial viscosity, respectively.

When the main agent is Epoxy Resin B, use of any catalysts

leads to storage stability lower than the case of Epoxy Resin A, and 2a gellates in second day and 2f in fourth days. However, 3 is not observed to have gellation for a short period of time, and the pot life of 3a is more than two months, that of 3b about six weeks, and even 3c about one month.

As discussed above, benzylmethylsulfonium salt (2a) exhibits a practical pot life at a limited storage temperature (20°C or less) and dimethylsulfonium salts (3) even at 40°C, and therefore they have been shown to function as industrially useful thermally latent curing catalysts.

3.2 Evaluations as Photolatent Curing Catalysts

The reports ¹⁵⁻²⁰⁾ said that the sulfonium salts not only act as thermally latent curing agents, but also are photolatent catalysts capable of initiating PGE polymerization by generating cation species via UV irradiation. Thus, a composition obtained by adding each sulfonium salt to Epoxy Resin B, an effective vehicle for ultraviolet curing, was applied to the surface of a hard vinyl chloride plate. The coat was irradiated with UV by means of a high-pressure mercury lamp to measure the amount of irradiation required for curing of the coat, i.e. curing energy.

As a result, sulfonium salt (2f) having a nitro group at the p-site of benzene ring of the benzyl group is shown to have a high activity similar to that of SP-170 (manufactured by Asahi

Denka Kogyo K.K.) commercially available as a photolatent curing catalyst (Table 7). In addition, the other sulfonium salts, though having low activity relative to 2f, cure a coat using UV irradiation and the order of activity is as follows: 2f > 2a > 3a > 3b. However, as described in the previous paragraph of Storage Stability, the compositions prepared by the addition of 2a and 2f in Epoxy Resin B are poor in pot life, and so the storage of them in the form of a one-component composition needs a dark place and a low temperature considerably.

Table 6 Storage stability of epoxy compositions with sulfonium salts at 40°C.

Epoxy resin	Storage time (day) ^{a)}	Viscosity (cps) / 25°C				
		2a	2f	3a	3b	3c
A	Initial	4100	4100	4100	4100	4100
	1	19000	4500	4100	4100	4100
	2	19500	5100	4100	4100	4100
	4	Gel	7900	4100	4100	4200
	10		21000	4100	4100	4400
	20		Gel	4100	4100	5000
	30			4200	4900	5500
	60			4300	5000	7600
B	Initial	230	230	230	230	230
	1	2400	990	230	230	230
	2	Gel	3600	230	230	250
	4		Gel	230	230	250
	10			250	250	280
	20			250	300	340
	30			280	350	410
	60			300	500	630

Composition: Epoxy resin A / PGE / Sulfonium salt = 88 / 12 / 1
Epoxy resin B / PC / Sulfonium salt = 100 / 2 / 1

a) Stored in the dark

Table 7 Curing energy required for epoxy resin B compositions with sulfonium salts by photoirradiation.

Composition (weight ratio)			Energy (mJ / cm ²)
Sulfonium salt	PC	Epoxy resin B	
2a / 1.5	3	100	138
2f / 1.5	3	100	34
3a / 1.5	3	100	195
3b / 1.5	3	100	277
SP-170 ^{a)} / 3			34

a) Photolatent catalyst manufactured by Asahi Denka Kogyo K. K.

On the other hand, compositions using 3a and 3b have long pot lives when stored in a dark place even at 40°C and are shown to function as thermally latent and photolatent curing catalysts for epoxy resins. Additionally, the special activity of 2f is attributable to the shoulder peak of UV absorption present in the wavelength range of 350 to 385 nm²⁰⁾, and it is supposed to effectively form cation species via the i line (bright line at 365 nm) of a high-pressure mercury lamp.

4. Conclusion

As discussed above, it has been shown that benzylmethysulfonium and p-nitrobenzylmethysulfonium salts having a phenol structure on their sulfur atom (2a, 2f) and dimethysulfonium salts (3a to 3c) function as thermal latent curing catalysts for epoxy resins, as well as photolatent curing catalysts. Thus, they can be applied as unique cation generating agents. Furthermore, benzylmethysulfonium salts (2c, 2d, 2e) of high activities enable curing reaction at room temperature to about 40°C, although they cannot be expected to have a merit of one-component. They are moisture absorption-free, stable crystals of easy handling and thus are useful as cation type curing catalysts. Additionally, epoxy resin compositions containing 2a and 2f are poor in pot life and so they are presently under various investigations for improvement.

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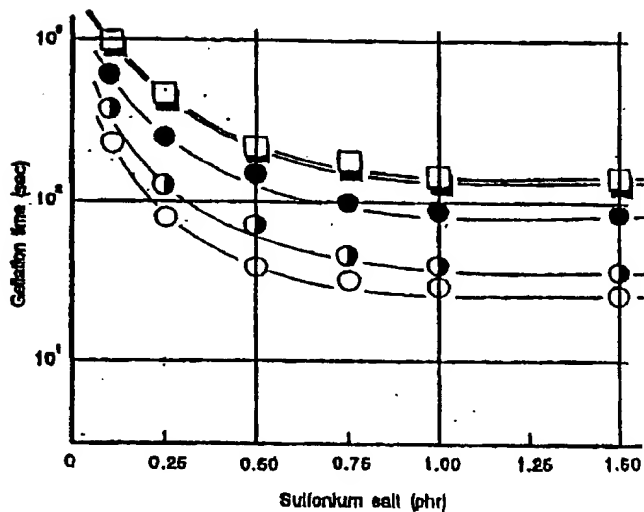


Fig. 1 Gellation time versus amount of sulfonium salt in curing of epoxy resin A composition.

Solution of catalyst : PO / Sulfonium salt = 2 / 1

- ● - : 2a / 130°C - ○ - : 2f / 170°C - □ - : 3b / 190°C
 - ○ - : 2a / 150°C - ■ - : 3c / 180°C

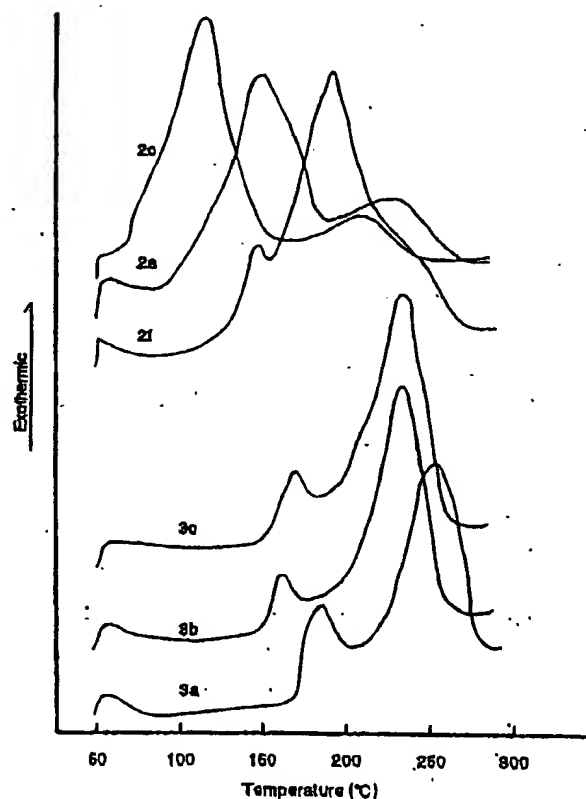


Fig. 2 DSC curves of compositions of epoxy resin A with sulfonium salts.

Composition : Epoxy resin A / PO / Sulfonium salt = 100 / 1 / 0.5
Scan speed : 10°C / min

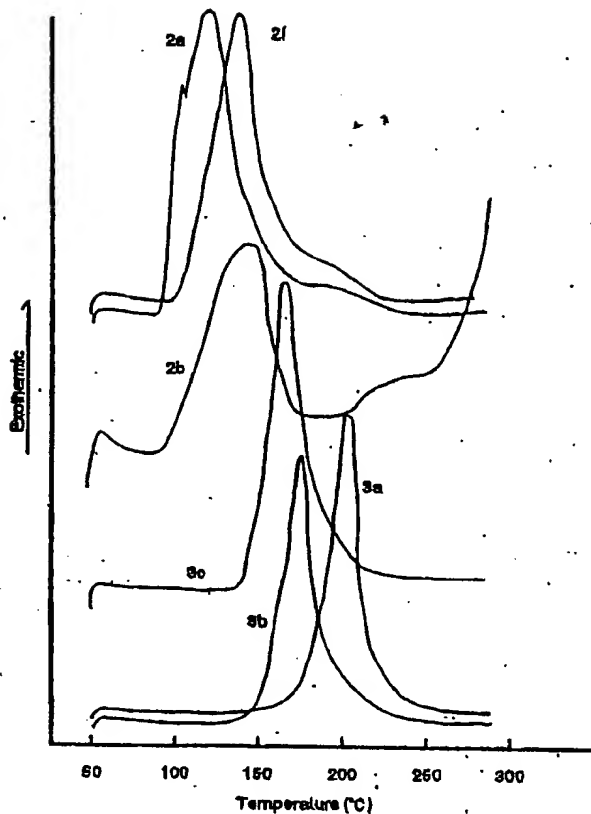


Fig. 3 DSC curves of compositions of epoxy resin B with sulfonium salts.

Composition: Epoxy resin B / PC / Sulfonium salt = 100 / 1 / 0.5
Scan speed: 10°C / min

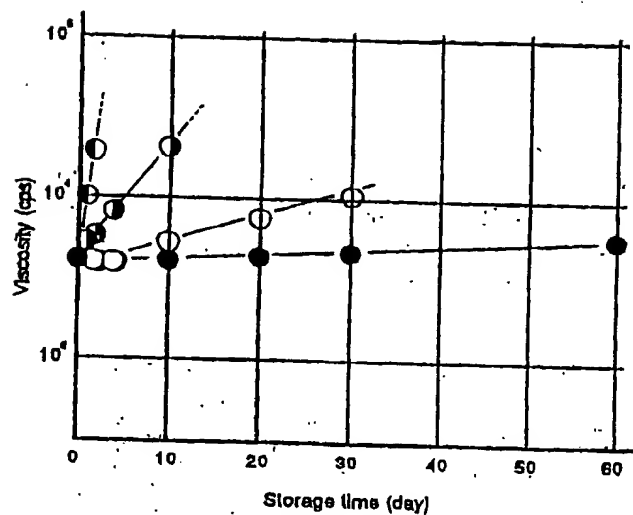


Fig. 4 Storage stability of composition of epoxy resin A with 2a at various temperatures.

Composition: Epoxy resin A / PC / 2a = 100 / 2 / 1
Viscosity: Measured at 25°C

—●—: 10°C —◐—: 30°C
—○—: 20°C —◑—: 40°C